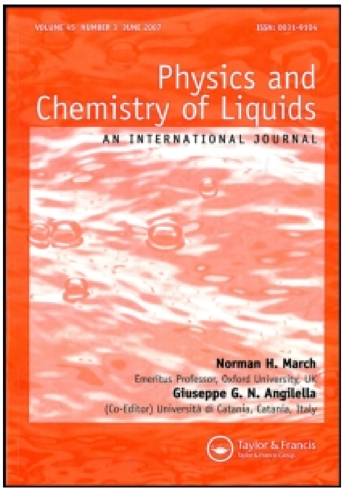

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Synergism in cationic gemini - additive systems

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Synergism in cationic gemini – additive systems

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A series of dicationic gemini surfactants with the general formula $C_{16}H_{33}(CH_3)_2N^+{-}(CH_2)_s{-}N^+(CH_3)_2C_{16}H_{33}$, $2Br^-$ (where $s = 4$–6), designated as 16-*s*-16, were synthesised. Their interaction with organic additives: *n*-alcohols (C_3H_7OH, $C_7H_{15}OH$, $C_8H_{17}OH$) and the corresponding amines ($C_3H_7NH_2$, $C_7H_{15}NH_2$, $C_8H_{17}NH_2$) in the absence and presence of KNO_3 at 30°C was studied viscometrically to observe their effect on assembly formation and micellar transition. The simultaneous presence of KNO_3 and organics induced rich aggregates morphologies in the gemini micellar systems by giving high viscosity values. On comparing the behaviour of the gemini surfactant series for a given alkyl chain length of the organic additive, the spacer is found to markedly influence the behaviour; shorter the spacer, earlier the sphere-to-rod transition. In the case of the conventional surfactant, CTAB, the concentration of KNO_3 used with the geminis was insufficient to induce any transition.

Keywords: geminis; additives; salt; alcohols; amines; viscosity

1. Introduction

This article is a part of a study of the effect of additives (salt, alcohols, etc.) on gemini micellar transitions. Normal surfactant molecules have a single hydrophobic tail, connected to a hydrophilic head. To gain better insight into micellisation, novel surfactants with unusual structures were synthesised. In recent years, the gemini surfactants have proved themselves ‘unique’ to the world of surfactants [1] due to their greater efficiency and effectiveness over comparable conventional surfactants which make them more cost-effective as well as environmentally desirable. They have two chains linked at the head group level by a hydrophobic or hydrophilic spacer. Due to the presence of the dimeric segments in the surfactant molecule, they exhibit unusual physicochemical behaviour. Their structure, together with their low critical micelle concentration (cmc) values, make them very efficient at reducing surface tension, leading to potential applications such as detergents, dispersants, antifoaming agents, fabric softeners, etc. [2–5]. The more interesting properties in comparison to ‘monomeric surfactants’ are mainly related to the distribution of distances between head groups [6]. Because of the spacer group, the repulsion between the head groups can be reduced, which brings them closer to each other. Thus, a gemini surfactant with a short spacer group is better. A very special feature of these

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surfactants is the ability to design their physicochemical properties and molecular structure by altering the spacer and alkyl chains. Besides the molecular structure of geminis, the aggregates are sensitive to the change of various environmental factors, such as concentration, additives (salt, alcohol, etc.), temperature, pH and so on.

In response to the increasing demands of high-performance surface active compounds, the surfactant-additive systems have been explored widely in the past using different techniques [7–12]. As far as geminis are concerned, there still is room for gemini-additive systems. Gemini-additive assemblies often play an important role in micellar transition. Such systems demonstrate very strong synergism when mixing dimeric surfactants with organic additives. The association behaviour is strongly enhanced due to the dimerisation in geminis compared to monomeric analogue.

Thus, pursuant to the continued research in this area [13–16], we have investigated the effects of organic additives: *n*-alcohols (C_3H_7OH, $C_7H_{15}OH$, $C_8H_{17}OH$) and the corresponding amines ($C_3H_7NH_2$, $C_7H_{15}NH_2$, $C_8H_{17}NH_2$) with dicationic gemini surfactants with the general formula $C_{16}H_{33}(CH_3)_2N^+{-}(CH_2)_s{-}N^+(CH_3)_2C_{16}H_{33}$, $2Br^-$ (where $s = 4$–6) in the presence and absence of inorganic salt KNO_3 at 30°C by viscometry. The aim of this work is to explore the micellar transitions as a consequence of synergistic effect in gemini micellar solutions. For comparison, the effect was observed for the parent 'monomeric' compound cetyltrimethyl ammonium bromide (CTAB) too.

2. Experimental section

All gemini surfactants (symbolised as 16-*s*-16. $s = 4$–6) were prepared and characterised as described in previous papers [4,17]. Potassium nitrate (KNO_3, ≥98%), 1-propanol (C_3H_7OH, ≥99%), 1-heptanol ($C_7H_{15}OH$, >99%) were purchased from Merck, whereas octanol ($C_8H_{17}OH$, >97%) and all the amines (*n*-propylamine, $C_3H_7NH_2$; *n*-heptylamine, $C_7H_{15}NH_2$; *n*-octylamine, $C_8H_{17}NH_2$ all 'purum grade') were obtained from Fluka (Buchs, Switzerland). The details of the experimental procedure, were the same as in previous studies [13]. The viscosity measurements were carried out with a Ubbelohde viscometer thermostated at $30°C \pm 0.1°C$. The method of measurements of viscosities under Newtonian flow conditions was the same as described in the literature [18]. The solvent flow time in the viscometer was always longer than 200 s and no kinematic corrections were introduced [19]. The average of three consecutive measurements was considered for each run. The results were associated with a standard deviation of ±5%.

3. Results and discussion

The inorganic salts are mainly considered as thickening agents for surfactant solutions. The effect of the inorganic salts on ionic surfactant solutions have been discussed in terms of electrostatic interactions, changes in water structure, ionic hydratability, etc. [20–24].

First of all, the spacer effect of gemini surfactants on the micellar growth was studied in the 16-*s*-16 series in the absence of any additive. With the spacer increasing, the viscosity values obviously decreased, which confirms the ability of short spacer geminis ($s = 4$) to show sphere-to-rod transitions at fairly low concentrations [25]. From this, we were able to choose a concentration of surfactants on which further studies could be performed. The increase in relative viscosity (η_r) was, however, marginal in the case of the monomeric counterpart, CTAB (Figure 1).

The effect of adding the inorganic salt (KNO_3) to the micellar solutions was more or less similar, albeit a higher magnitude of η_r (Figure 2). By the addition of KNO_3, the bound counterions screen the electrostatic repulsion between the ionic head groups. This results in tighter packing, which modifies the spontaneous curvature of the surfactant assemblies and the solution properties, in the present case the η_r. The rich aggregation behaviour can be attributed to the special molecular structure of geminis and the appropriate interaction with the KNO_3. In the conventional surfactant (where, no doubt, the screening effect is present), the head groups are randomly distributed on the surface separating the aqueous phase and the micelle hydrophobic core. Due to the active opposite forces in the process of micelle formation, the distances between the head groups are maximum at a thermodynamic equilibrium distance. In geminis the distribution of distances becomes bimodal. The presence of spacers overcomes the electrostatic repulsion between the head groups and make them closer to each other [26]. Therefore, it is expected to strongly affect the curvature of the surfactant layer, and thus the micelle shape and the properties of the solutions. The salt addition influences this distribution and also the optimum area per head group (A_o) with a simultaneous increase in the Mitchell–Ninham parameter [27], R_P ($v/A_o l_c$, v and l_c are, respectively, the volume and length of the surfactant monomer). This is the reason for the sphere-to-rod transition being more pronounced with geminis of shorter spacer, giving rise to higher η_r values. As can be seen from Figure 2, no effect was observed with CTAB micelles for the same concentration range. Therefore, further studies on CTAB micelles were discontinued.

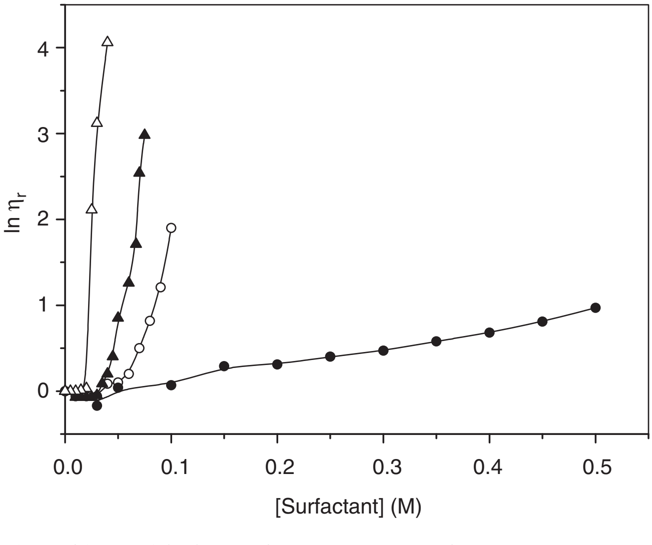

Figure 1. Variation of ln η_r with the [surfactant]: 16-4-16 (Δ); 16-5-16 (▲); 16-6-16 (○); CTAB (●). Lines are drawn as a guide to the eye.

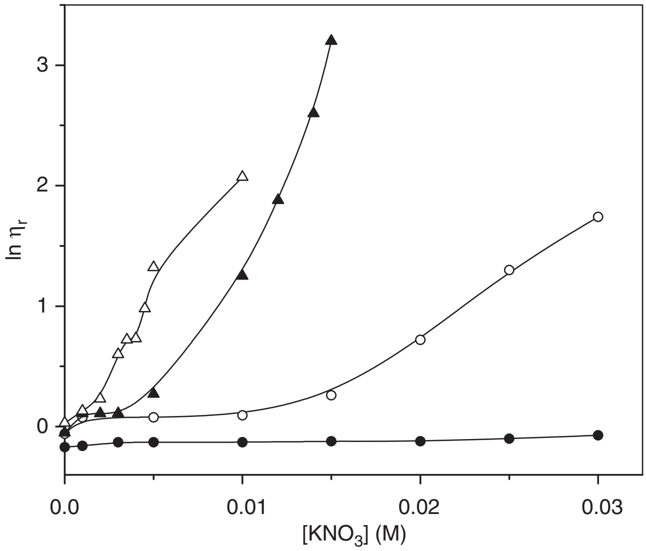

Figure 2. Variation of ln η_r with the [KNO_3] to surfactant solutions: 0.02 M 16-4-16 (Δ); 0.03 M 16-5-16 (▲); 0.03 M 16-6-16 (○); 0.03 M CTAB (●). Lines are drawn as a guide to the eye.

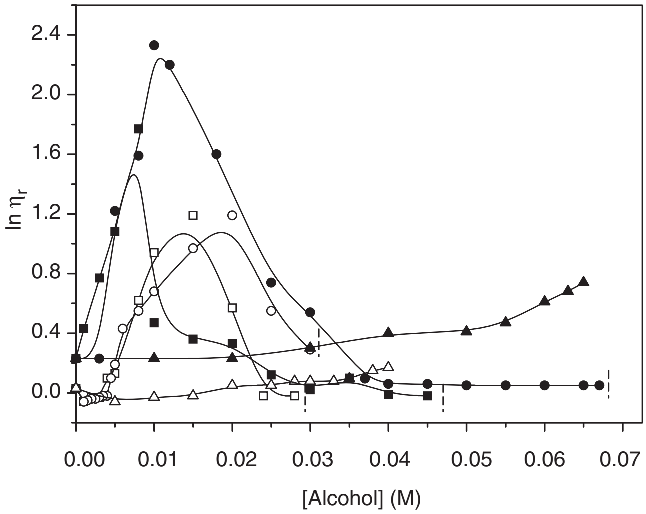

Figure 3. Variation of ln η_r with the added [alcohol] to 0.02 M 16-4-16 solutions in the absence (open symbols) and presence (filled symbols) of 0.002 M KNO_3 at 30°C (up to the solubility limit indicated by dotted lines): C_3H_7OH (▲); $C_7H_{15}OH$ (●); $C_8H_{17}OH$ (■). Lines are drawn as a guide to the eye.

In order to observe the role of alcohols, the effect was studied at 30°C (Figures 3–5). We see that the effects are totally dependent on the alcohol's alkyl chain. The shorter chain alcohol (C_3H_7OH) has no effect on the η_r values leading to no change in the micellar growth, because short chain alcohols are known to inhibit

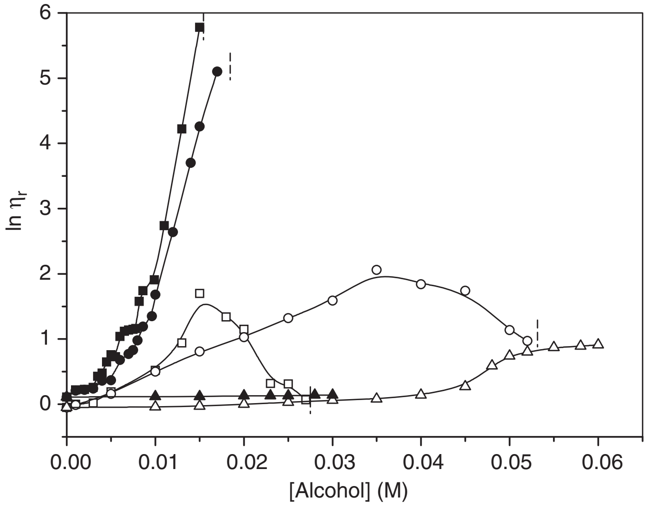

Figure 4. Variation of ln η_r with the added [alcohol] to 0.03 M 16-5-16 solutions in the absence (open symbols) and presence (filled symbols) of 0.005 M KNO_3 at 30°C (up to the solubility limit indicated by dotted lines): C_3H_7OH (▲); $C_7H_{15}OH$ (●); $C_8H_{17}OH$ (■). Lines are drawn as a guide to the eye.

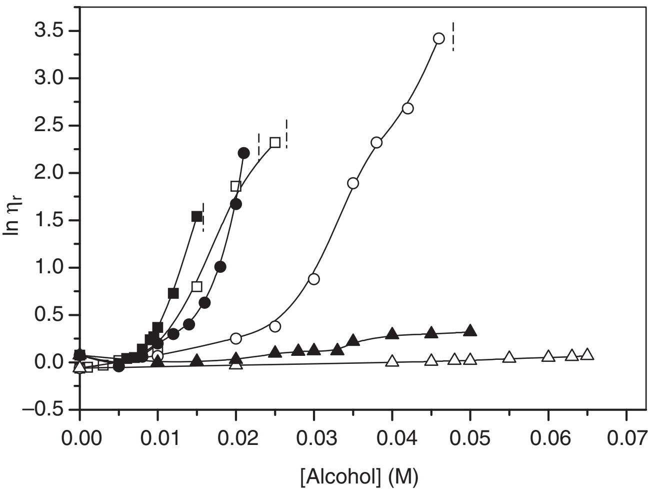

Figure 5. Variation of ln η_r with the added [alcohol] to 0.03 M 16-6-16 solutions in the absence (open symbols) and presence (filled symbols) of 0.005 M KNO_3 at 30°C (up to the solubility limit indicated by dotted lines): C_3H_7OH (▲); $C_7H_{15}OH$ (●); $C_8H_{17}OH$ (■). Lines are drawn as a guide to the eye.

the surfactant molecules from penetrating into the micelles [28]. Also, C_3H_7OH is hydrophilic in nature and continues to remain in water, not in the aggregated structure (micelles). As a result, no change in the η_r values is observed in this case. Indeed, the heptanol and octanol influence sphere-to-rod transition. This transition modifies mainly the packing structure which, in turn, changes the solution viscosity.

The longer chains of alcohols tend to be located in the micellar core, which is occupied by the hydrophobic part of the surfactant molecules and thus alcohol-surfactant mixed micelles [29] are likely to be formed. The –OH group of these alcohols aligns parallel to the surfactant molecule and thus it is faced towards the water phase by forming easily the alcohol-surfactant mixed micelle. Due to this tendency, the head group repulsion is minimised. As a result, surface area per head group (A_o) is decreased and the R_P is increased [30]. Thus, viscosity changes are observed in the order $C_3H_7OH < C_7H_{15}OH < C_8H_{17}OH$ (Figures 3–5). In the dilute concentration regions of geminis with short spacers ($s=4$ and 5), the addition of alcohols induces the viscosity of the gemini micellar systems to go through a marked maximum. Previous studies [25] have shown that alcohols being located in the interfacial region of surfactant micelles promote the micelles to be larger at their lower concentrations. Due to this process, the viscosity of the system rises. With continuously increasing alcohol content, it gets solubilised in the palisade of the micelles and induces these rod-like micelles to be transformed into smaller ones showing a decrease in η_r values.

Figures 6–8 show that in case of corresponding amines, the viscosity does not change much with $C_3H_7NH_2$, but a distinct rise is observed with the higher chain amines ($C_7H_{15}NH_2$, $C_8H_{17}NH_2$). These amines have been found to be solubilised in micelles by electrostatic (because of the feeble hydrolysis, amine group is protonated: $-RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$) and hydrophobic effects, and the amine groups are left on the surface of the micelle [13,14,31]. The solubilisation (rather intercalation) of amine in gemini micelles reduces the electrostatic repulsion between the gemini head groups, thereby promoting micellar growth. The availability of amine causes decrease in A_o with a concomitant decrease in surface charge density and increase in the Mitchell–Ninham parameter R_p [27]. Also, because of the intercalation of the protonated amine, the alkyl moiety would be embedded into the

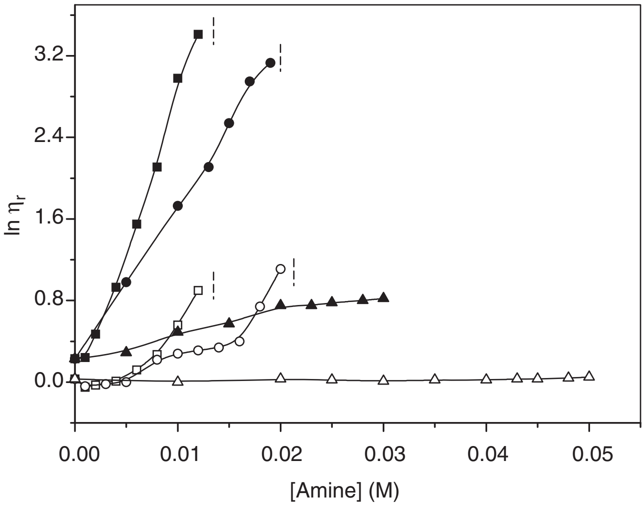

Figure 6. Variation of ln η_r with the added [amine] to 0.02 M 16-4-16 solutions in the absence (open symbols) and presence (filled symbols) of 0.002 M KNO_3 at 30°C (up to the solubility limit indicated by dotted lines): $C_3H_7NH_2$ (▲); $C_7H_{15}NH_2$ (●); $C_8H_{17}NH_2$ (■). Lines are drawn as a guide to the eye.

hydrophobic portion. This results in an increase in the volume of the micellar core (v_c), which increases R_p. Thus, gemini-amine have tendency to promote micellar growth as reflected by an increase in viscosity values (Figures 6–8).

To observe the role of the combined presence of KNO_3 and organic additives (alcohols and amines), we also investigated the gemini-additive systems in presence

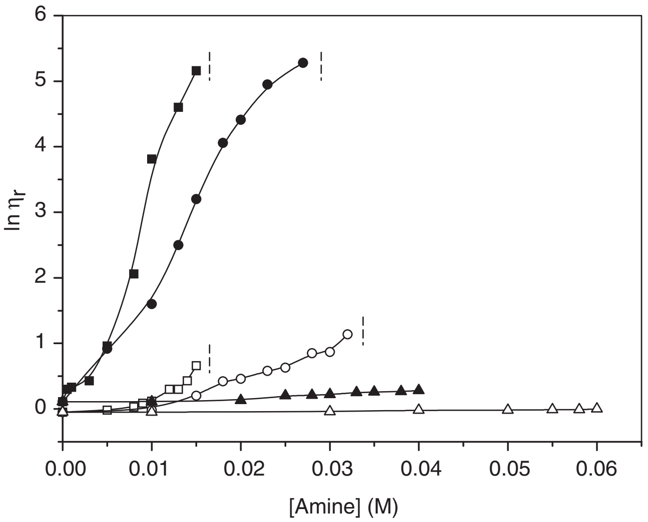

Figure 7. Variation of ln η_r with the added [amine] to 0.03 M 16-5-16 solutions in the absence (open symbols) and presence (filled symbols) of 0.005 M KNO_3 at 30°C (up to the solubility limit indicated by dotted lines): $C_3H_7NH_2$ (▲); $C_7H_{15}NH_2$ (●); $C_8H_{17}NH_2$ (■). Lines are drawn as a guide to the eye.

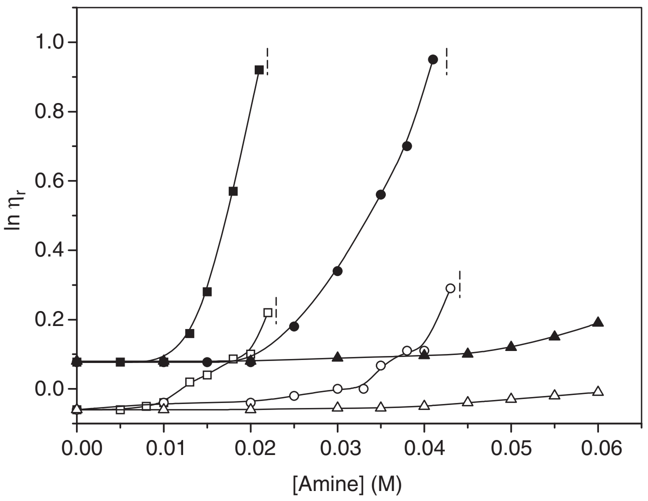

Figure 8. Variation of ln η_r with the added [amine] to 0.03 M 16-6-16 solutions in the absence (open symbols) and presence (filled symbols) of 0.005 M KNO_3 at 30°C (up to the solubility limit indicated by dotted lines): $C_3H_7NH_2$ (▲); $C_7H_{15}NH_2$ (●); $C_8H_{17}NH_2$ (■). Lines are drawn as a guide to the eye.

of KNO_3 at the same temperature (Figures 3–8). A significant viscosity increment of the system was observed. This confirms the existence of the novel phenomenon ‘synergism’ when salt and organic additives both are present in the micellar solution. The manifold increase of viscosity values is the consequence of different forces responsible for micellar growth. The addition of KNO_3 to gemini micelles weakens the Coulombic repulsion between the micelles and the interaction of organic additives decreases the intramicellar Coulombic repulsion and increases the hydrophobic interactions among monomers of gemini micelles. Both the decrease of Coulombic repulsion and/or increase in the hydrophobic interactions are favourable conditions for micellar growth of gemini micelles.

4. Concluding remarks

In an attempt to show how organic molecules can be used to explore their potential for viscosity enhancement in micellar media (which are in demand for various industrial applications or reaction media where lower ionic strength is required), the gemini–additive interaction is studied by examining the viscosity changes in these systems. It has been observed that the properties of aqueous solutions of gemini surfactants can be efficiently modified by the addition of KNO_3 or organic additives (alcohols or amines). The salt-induced transition of gemini micelles is not caused by the effect of structure of water, but it is brought about by the electrostatic effect of the added KNO_3. On addition of organic additives, long chain alcohols/amines enhanced the sphere-to-rod transition and reduced the threshold concentration for the onset. This was due to the formation of mixed micelles. The presence of KNO_3 and organic additives in the system produced favourable conditions which do not exist in the presence of either the salt or the organic additive alone. A stronger synergism occurred with the geminis. Thus, viscous solutions can be obtained for mixtures of geminis and additives at low concentrations, whereas no effect was observed for mixtures containing the analogous ‘monomeric’ surfactant CTAB in the same concentration range.

It is also evidenced from Figures 3–8 that the degree of effectiveness of the organic additive (be it the concentration for transitions or at the maxima) increases with increasing alkyl chain length; this indicates the importance of the hydrophobic interactions.

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